

# Meteoritic Amino Acids: Diversity in Compositions Reflects Parent Body Histories

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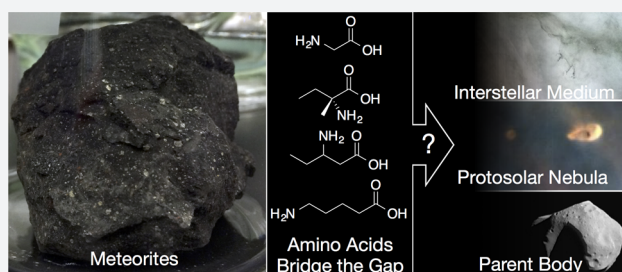
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**ABSTRACT:** The analysis of amino acids in meteorites dates back over 50 years; however, it is only in recent years that research has expanded beyond investigations of a narrow set of meteorite groups (exemplified by the Murchison meteorite) into meteorites of other types and classes. These new studies have shown a wide diversity in the abundance and distribution of amino acids across carbonaceous chondrite groups, highlighting the role of parent body processes and composition in the creation, preservation, or alteration of amino acids. Although most chiral amino acids are racemic in meteorites, the enantiomeric distribution of some amino acids, particularly of the nonprotein amino acid isovaline, has also been shown to vary both within certain meteorites and across carbonaceous meteorite groups. Large L-enantiomeric excesses of some extraterrestrial protein amino acids (up to ~60%) have also been observed in rare cases and point to nonbiological enantiomeric enrichment processes prior to the emergence of life. In this Outlook, we review these recent meteoritic analyses, focusing on variations in abundance, structural distributions, and enantiomeric distributions of amino acids and discussing possible explanations for these observations and the potential for future work.



## INTRODUCTION

Meteorites, the rocky remnants of asteroids or comets that land on Earth, serve as historians and messengers from the early Solar System. The organic contents of meteorites reflect a long and potentially diverse history, beginning with the formation of the Solar System in a molecular cloud in which low temperature radiation-driven chemistry and isotopic fractionation could occur in both the gas phase and in ices. Some of this molecular cloud material was incorporated into growing planetesimals where additional chemical reactions and processing took place. These planetesimals include the asteroids and comets that are the parent bodies of meteorites. Thus, meteoritic organic content reveals information not only about early solar system chemistry but also about the histories of parent bodies as recorded in the effects of physical and chemical processes that occurred over the past 4.5 billion years. Meteorites are also delivery vehicles, impacting the Earth with 40 million kg of cosmic material each year,<sup>1</sup> with a much higher flux earlier in the Earth's history; this material may have contributed to the inventory of organic compounds available for the origin of life.

Studies of the organic content of meteorites date to 1834,<sup>2</sup> with compound-specific measurements beginning in the 1960s.<sup>3</sup> Meteorite analyses reveal a major organic component of insoluble macromolecular material, as well as a complex and

highly diverse suite of soluble organics,<sup>4–6</sup> including aliphatic and aromatic hydrocarbons,<sup>7–12</sup> carboxylic acids,<sup>13–15</sup> hydroxy acids,<sup>16,17</sup> polyols,<sup>18</sup> amino acids,<sup>7,8,19–22</sup> and more.<sup>23–26</sup> Of these, amino acids have been of particular interest for several reasons. Amino acids are essential organic molecules as the monomers of proteins and enzymes in all life on Earth, making them targets for astrobiological studies. Analytical techniques exist for isolation and analysis of amino acids. Many amino acids are chiral, and the origin of homochirality of biological amino acids is a major question in origin of life research. They are also a constrained yet structurally diverse group of compounds. Figure 1 illustrates the 23 isomers and enantiomers of five-carbon aliphatic primary monoamino, monocarboxylic, non-heteroatom (hereafter “simple”) amino acids, highlighting differences in the position of the amine group relative to the acid group, as well as the structure of the carbon backbone. The structural, isotopic, and enantiomeric compositions of amino acids can be signatures of their formation mechanisms and processing histories.<sup>5,27,28</sup>

Meteorites are classified according to their petrologic characteristics (e.g., texture, mineralogy), whole-rock chemical composition, and oxygen-isotope composition.<sup>29</sup> One classification

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	$\alpha$ -amino isomer	$\beta$ -amino isomer	$\gamma$ -amino isomer	$\delta$ -amino isomer
<i>n</i> -				
<i>sec</i> -				* = chiral carbon
<i>iso</i> -				
<i>tert</i> -				
<i>sec</i> -				

**Figure 1.** Structure of amino acids can be classified according to the position of the amine relative to the acid (e.g., if the amine is on the  $\alpha$ ,  $\beta$ ,  $\gamma$ , or  $\delta$  carbon) and the structure of the aliphatic carbon backbone. For the five-carbon aliphatic primary monoamino, monocarboxylic, non-heteroatom amino acids shown here, there are 23 possible structural isomers and enantiomers. Understanding the distribution of these species can help elucidate the formation and processing histories of the meteorite in which they are found. These five-carbon compounds are particularly useful, as they provide a large suite of chemical isomers that can be individually quantitated by current analytical methods.

Recent amino acid results reveal differences between meteorite classes that have implications for our understanding of solar system and parent body chemistry, as well as for the contribution of meteorites to the origin of life on Earth.

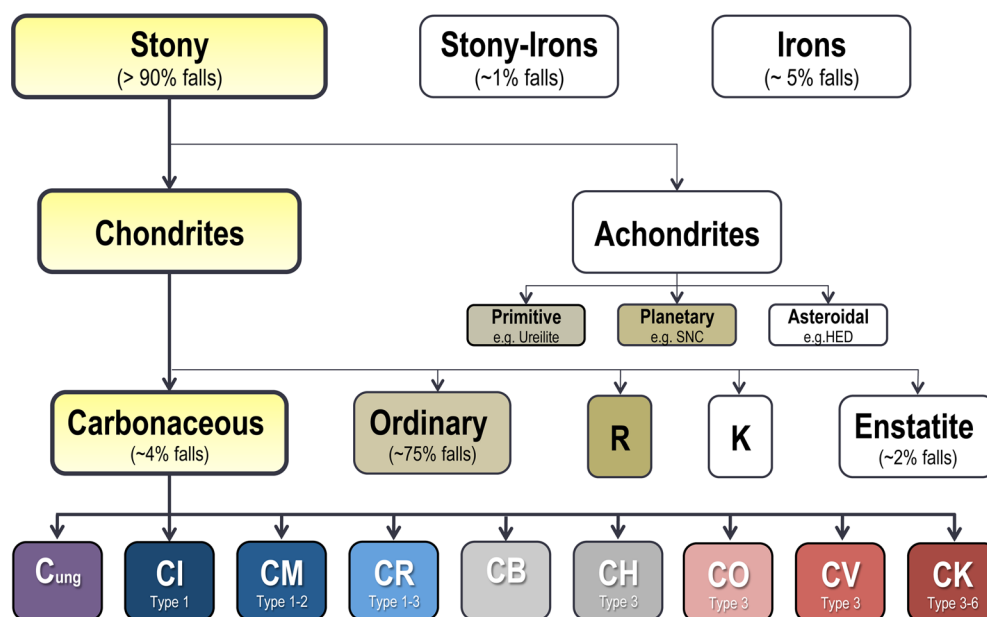
system yields 45 named groups of meteorites,<sup>29</sup> ranging from metallic meteorites composed almost entirely of iron and nickel metals from protoplanetary cores to primitive stony meteorites that have never been significantly heated; Figure 2 gives a partial overview of the classification scheme. There are also several meteorites that do not fit in the existing groups.

Most studies of meteoritic organics focus on what are known as “carbonaceous chondrites”, the class of primitive stony meteorites containing 2–5 wt % carbon.<sup>30</sup> Carbonaceous chondrites are divided into eight groups, each of which appears to derive from a different parent body, based on distinctive chemical and mineralogical compositions. These meteorites are further assigned petrographic types, depending on the type and extent of secondary processing they underwent in their parent bodies. Secondary processing includes the effects of the physical and chemical environment of the parent body, such as temperature (e.g., heating from radioactive species or from shock impacts)<sup>31</sup> and the amount of water present (caused by melting of ice accumulated during parent body formation).<sup>32</sup> Petrographic types range from 1 to 6, with 3.0 indicating minimal secondary processing, numbers less than 3.0 indicating increased aqueous alteration, and types greater than 3.0 indicating

increased thermal metamorphism; this system does not describe meteorites with both thermal and aqueous processing. As expected, both the composition of a meteorite and the conditions it experienced in its parent body have an observable effect on the amount and distribution of organic molecules in that meteorite. This has been particularly well documented for meteoritic amino acids.<sup>20–22,33–50</sup>

Early studies of meteoritic organics focused primarily on a few well-known, large meteorites. The year 1969 saw several important events, including the first Apollo Moon landings and the fall of two large carbonaceous chondrites: Murchison (CM2) and Allende (CV3). Each fall was seen as a brilliant fireball accompanied by earth tremors and a cloud of smoke, distributing >100 kg of fragments over a wide radius. Analytical laboratories preparing for the study of Apollo lunar samples eagerly investigated the organic contents of these two meteorites. The Murchison meteorite and other CM2 chondrites, such as the 12.6 kg Murray meteorite that fell in 1950,<sup>51</sup> dominated meteoritic amino acid analysis for decades, as shown in the distribution of literature reports depicted in Figure 3.

A shift in our understanding of meteoritic amino acids has occurred recently, partly enabled by an increasing supply of samples from carbonaceous chondrite groups and types other than CM2. The bulk of these meteorites are from Antarctica, where more than 22,000 meteorites have been collected to date on expeditions by the Antarctic Search for Meteorites (ANSMET) program,<sup>52</sup> a joint operation between NASA, NSF, and the Smithsonian Institution, with additional collection efforts by independent European- and Japanese-led searches. Improvements in analytical instrumentation have pushed detection limits ever lower and allowed for compound-specific stable isotopic measurements,<sup>53</sup> as well as analyses of very small samples of meteorites<sup>54</sup> and even milligram-sized Antarctic micrometeorites.<sup>55</sup>



**Figure 2.** This classification scheme divides into groups according to their petrologic characteristics, and also assigns petrographic types (1–6) representing their alteration history.<sup>29</sup> The abundance of the classes on Earth can be estimated by the percentage of meteorites discovered immediately after they fall to Earth (falls). To date, amino acids have been measured in representatives from all groups shown in this figure except those shown in white.

Recent amino acid results reveal differences between meteorite classes that have implications for our understanding of solar system and parent body chemistry, as well as for the contribution of meteorites to the origin of life on Earth. This new information on the diversity of meteoritic organic molecules highlights several areas that are ripe for further investigation. Two topics of particular interest are (1) understanding the signatures of formation mechanisms and processing histories preserved in meteoritic amino acids and (2) understanding the creation and amplification of observed amino acid enantiomeric excesses and exploring the implications for the origin of biological homochirality. Here, we discuss the current state and future opportunities in these areas.

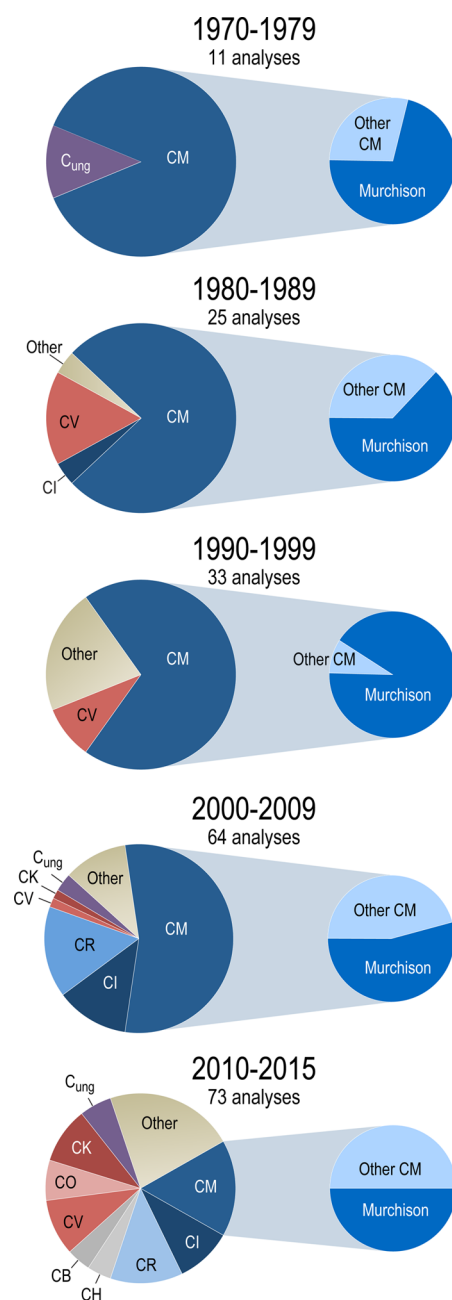
**Amino Acid Distributions. Signatures of Formation Mechanisms and Processing Histories.** Extensive investigations of Murchison over the past 45 years have shown it to be particularly rich in soluble organic materials,<sup>6</sup> including part-per-million (ppm) levels of the most abundant individual compounds among a suite of >70 named amino acids ranging from two to ten carbons in length, and including eight proteinogenic amino acids.<sup>41,56</sup> The amino acids in Murchison are predominantly  $\alpha$ -amino isomers, though appreciable levels of other isomers are present. The large available sample mass of Murchison and its relatively high abundances of amino acids have enabled its study by many researchers. This led to an overrepresentation of Murchison in meteorite literature (Figure 3) and the development of a paradigm in which the distribution of amino acids observed in Murchison was until recently considered typical for all meteorites. Even today, Murchison is still often viewed as the archetype to which other meteorites are compared.

As Figure 4 illustrates, however, analyses of aqueous extracts of meteorites from different groups and petrographic types reveal that the Murchison-like distribution of amino acids, with ppm concentrations and mainly  $\alpha$ -amino isomers, appears to be limited to a narrow range of CM2, CR2, and CR3 chondrites.

Meteorites that experienced greater aqueous alteration without accompanying high-temperature thermal alteration, such as the CI1, CM1, and CR1 chondrites, have lower abundances of amino acids and increased relative amounts of simple  $\beta$ -,  $\gamma$ -, and  $\delta$ -amino acid isomers.<sup>20,41,47</sup> Carbonaceous chondrites exposed to aqueous alteration as well as higher temperatures up to 400–600 °C (e.g., certain thermally altered CI1 chondrites or the Sutter's Mill CM2 chondrite) contain even lower abundances of amino acids,<sup>47,50,57</sup> perhaps unsurprising given that most amino acids start to thermally decompose above 150 °C in the solid state.<sup>58,59</sup>

The variety and complexity of meteoritic organics is becoming clearer as more meteorites are studied. In addition to further studies of meteorites, sample return missions to comets and asteroids will be of critical value.

CH3 chondrites, which contain ~20% metal by volume, have similar levels of amino acids to Murchison, but with much higher relative abundances of  $\beta$ -,  $\gamma$ -, and  $\delta$ -amino acids.<sup>46</sup> CB chondrites, with 60–80% metal by volume, have an order of magnitude lower amino acid abundance than CH chondrites, and contain a higher fraction of straight-chained amino acids with the amine group located on the carbon farthest from the carboxylic acid (*n*- $\omega$ -amino acids).<sup>46</sup> Meteorites that experienced more parent body heating, including the moderately heated CV3 and CO3 chondrites, as well as the more extensively heated CK4–CK6 chondrites are dominated by *n*- $\omega$ -amino acids, particularly the  $\delta$ -amino C<sub>5</sub> isomer.<sup>44,45,48</sup> Certain other meteorites that experienced high temperatures, such as intensely heated ureilites<sup>44</sup> and the Martian meteorite Roberts Massif 04262,<sup>60</sup> also contain low levels of mostly



**Figure 3.** An examination of published literature reports of meteoritic amino acid analyses, shown as proportion of total analyses by meteorite group (left) and proportion of CM analyses of Murchison vs other CM meteorites (right), illustrates the domination of Murchison and CM analyses until recent years. [Data taken from SI Web of Science search through 2015 with the search terms TS = (meteorit\* or chondrite) and TS = (amino and acid) refined by document types (article or letter). Only manuscripts including new amino acid data were included.]

*n*- $\omega$ -amino acids, while other heated meteorites such as LL3 ordinary chondrites have a different amino acid distribution.<sup>45</sup>

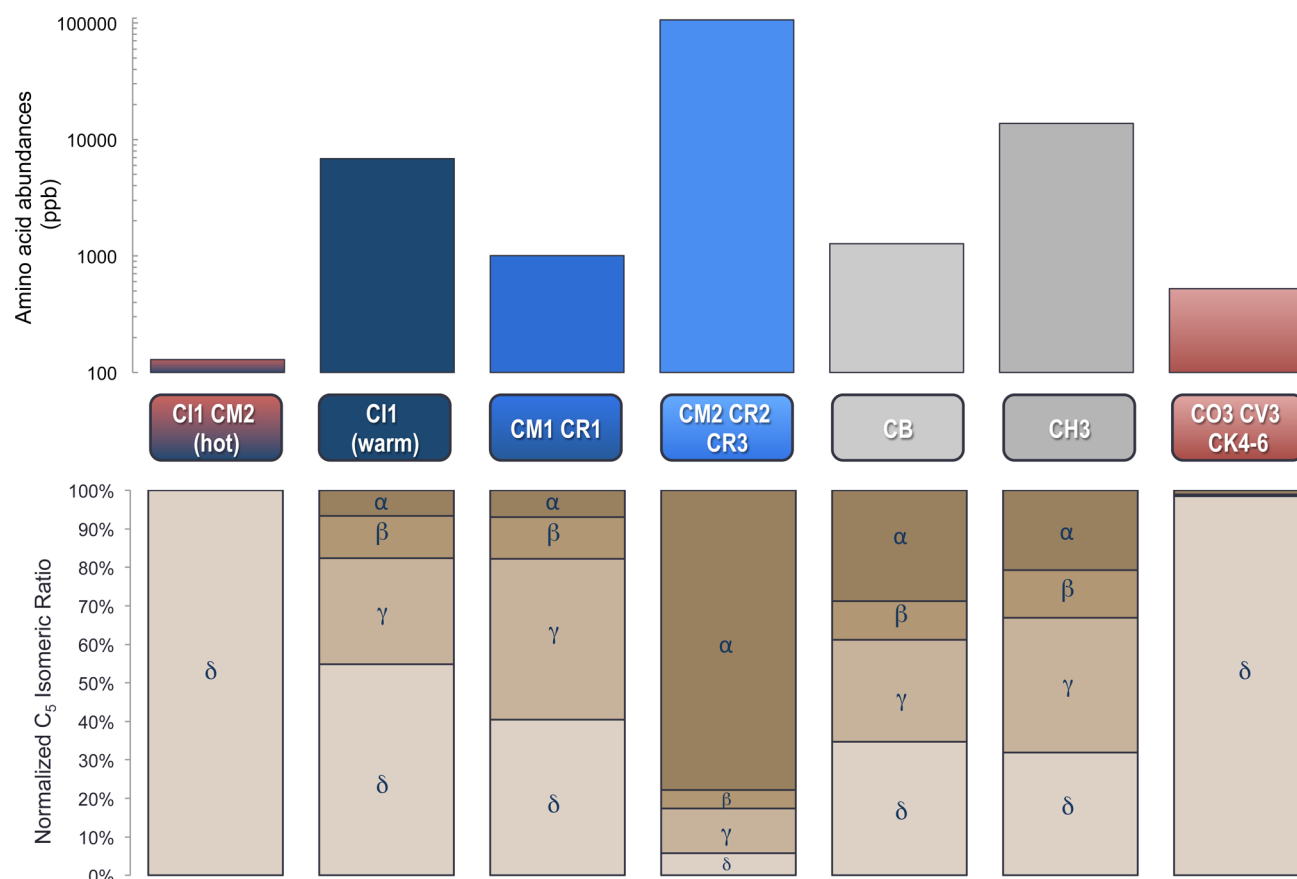
It appears that abiotic amino acid formation chemistry, as preserved by meteorites, is strongly dependent on the availability of amino acid precursors, temperature and water activity, and the mineralogical composition of the parent body. These factors influenced the abundances as well as the structural, enantiomeric, and isotopic composition of meteoritic amino acids. The ways in which these influences operated, however, are only beginning to be elucidated.

The diversity observed in meteoritic amino acids suggests multiple formation mechanisms in the early solar system and in parent bodies. In particular, the abundance of  $\alpha$ -amino acids in Murchison and other moderately aqueously altered meteorites is consistent with Strecker-type syntheses (Figure 5, bottom pathway).<sup>61</sup> Further support is also provided by the presence and similar distribution of  $\alpha$ -hydroxy acids in Murchison that form by the parallel cyanohydrin reaction (Figure 5, top pathway) as well as analogous iminodicarboxylic acids.<sup>61,62</sup>  $\beta$ -Amino acids cannot be produced through the Strecker mechanism, but it has been postulated that they formed through Michael addition of ammonia to  $\alpha,\beta$ -unsaturated nitriles.<sup>25,63</sup> Because Michael addition requires the presence of liquid water, it has been seen as a plausible explanation for the high levels of  $\beta$ -amino acids observed in some heavily aqueously altered meteorites (e.g., Orgueil and Ivuna, CI1);<sup>20</sup> aqueous alteration and oxidation also lead to preferential destruction of the more soluble and polar  $\alpha$ -amino acids.<sup>22</sup> The origin of  $\gamma$ - and  $\delta$ -amino acids is less certain, but they could plausibly form from decarboxylation or deamination of dicarboxylic or diamino acids<sup>53,64,65</sup> and may also form via photochemically produced radicals in pre-parent body environments, such as on the surfaces of interstellar icy grains.<sup>66–68</sup> The dominant distribution of *n*- $\omega$ -amino acids in thermally altered meteorites may be the result of so-called Fischer–Tropsch-type (FTT) reactions occurring between trapped cooling gases and catalytic mineral surfaces.<sup>44,69–71</sup>

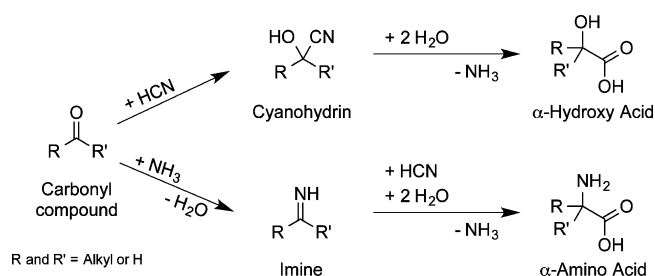
Although several formation mechanisms have been suggested for meteoritic amino acids, laboratory studies in this area have focused primarily on the mechanisms most relevant to the more heavily studied aqueously altered meteorites, such as Strecker-type syntheses leading to  $\alpha$ -amino acids. Future work is needed to assess the formation potential of other mechanisms, such as the FTT reactions, as well as the effects of alteration conditions on amino acid preservation and formation. Production of amino acids in laboratory analogue reactions and measurement of structural distributions and isotopic fractionation to compare with meteoritic data would help constrain chemical environments in the early solar system and in parent bodies.

Studying the meteoritic abundances and distributions of compounds related to amino acids may also provide insight into the formation of soluble meteoritic organics. Such compounds include hydroxy acids, carboxylic acids, and amines. Like amino acids, these compounds have the advantage that they are soluble, extractable, and stable under conditions necessary for analysis. These compounds' aliphatic moieties may originate from precursors common to amino acids as well, via ion/radical or photochemical reactions in the gas phase or on icy grain surfaces in interstellar or protostellar nebulae, and subsequent modification during and after accretion of the meteorite parent body.<sup>25,72</sup> Hydroxy acids may be the most closely related compounds to amino acids in the carbonaceous chondrites, as Strecker-type synthesis would produce both  $\alpha$ -hydroxy and  $\alpha$ -amino acids, with the relative abundance of each depending on the ratio of available H<sub>2</sub>O to NH<sub>3</sub> (Figure 5). Thus, the hydroxy to amino acid ratio in a meteorite may provide information on parent body conditions.<sup>61</sup> This ratio has been studied in only a few exclusively CM and CR meteorites, with results suggesting some common precursors and a dependence on the concentration of parent body ammonia in determining the relative abundance of amino and hydroxy acids.<sup>16,17</sup> Future comparisons of the molecular distributions of these compounds across more meteorites may constrain the contribution of parent body Strecker-type syntheses versus other synthetic routes.



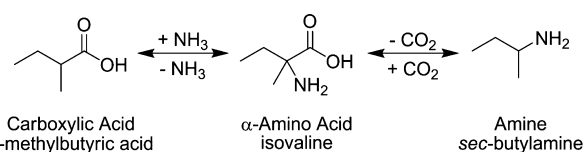


**Figure 4.** Average total amino acid abundances (top) and structural distributions of amine position in C<sub>5</sub> amino acids (bottom) in carbonaceous chondrites vary greatly with class and petrographic type. Structural distributions are shown as relative abundances of isomers of C<sub>5</sub> amino acids, normalized to the total number of possible isomers (i.e., random selection of amine position during formation should produce 25% each of α, β, γ, and δ isomers in this plot). A “sweet spot” of high abundance and high relative abundance of α-amino acid isomers, such as those used in terrestrial biology, is observed in the cool, moderately aqueously altered meteorites such as the Murchison CM2. Data is taken from selected meteorites analyzed by the authors using the same workup and analysis methods for all samples.<sup>39,41,44,46–48,57</sup>



**Figure 5.** Strecker-cyanohydrin synthesis can produce either α-hydroxy acids (top pathway) or α-amino acids (bottom pathway), depending on the availability of ammonia.

Carboxylic acids and amines can interconvert to amino acids through the addition or loss of CO<sub>2</sub> or NH<sub>3</sub> (Figure 6). They may also share common precursors with amino acids, such as aldehydes, ketones, and nitriles. Abundances of these compounds vary, with carboxylic acids among the most abundant soluble compounds in CM2 chondrites, but present in only low concentrations in CR2 meteorites.<sup>15,38,73</sup> Similarly, amines are more abundant than amino acids in CM2 chondrites, but less abundant in CR2 meteorites.<sup>38,40</sup> The molecular distributions of all of these compounds in CM2 and CR2 chondrites follow similar trends, decreasing in concentration with increasing molecular weight.<sup>15,74,75</sup> Additionally, amines and amino acids both favor structures with the amino group on secondary



**Figure 6.** Amino acids may interconvert with carboxylic acids through loss or addition of NH<sub>3</sub>, and with amines through loss or addition of CO<sub>2</sub>, shown here with the amino acid isovaline and its analogous carboxylic acid (2-methylbutyric acid) and amine (sec-butylamine).

carbons relative to other structural isomers.<sup>74,75</sup> These similarities between carboxylic acids, amines, and amino acids suggest that meteoritic aliphatic organics may have been synthesized (or destroyed) through similar processes that yielded a full suite of structural isomers; future studies of these compounds across additional carbonaceous chondrite groups and types will aid in understanding these formation processes.

The variety and complexity of meteoritic organics is becoming clearer as more meteorites are studied. In addition to further studies of meteorites, sample return missions to comets and asteroids will be of critical value. Missions such as NASA's OSIRIS-REx<sup>76</sup> and JAXA's Hayabusa2<sup>77</sup> will provide samples from primitive bodies with greater contextual information than typically studied meteorites.<sup>76</sup> Careful contamination control will result in minimal contamination, and the analysis and

archiving of spacecraft components and witness materials will provide unprecedented knowledge of any terrestrial contributions to these samples.

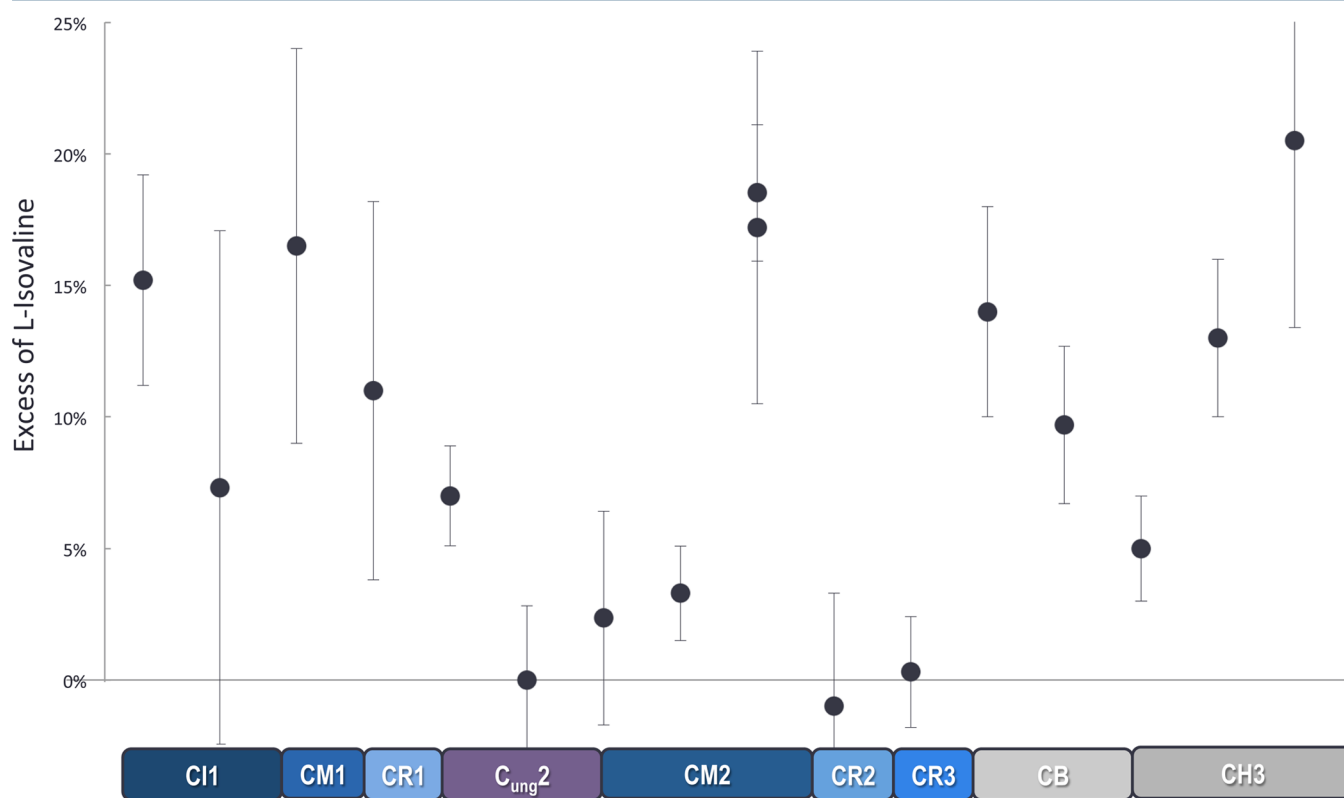
**Enantiomeric Excesses. Formation, Amplification, and Potential Relevance to Origin of Homochirality.** Meteoritic amino acid studies also focus on enantiomeric compositions, which are important in elucidating a contribution to the origin of biological homochirality, as well as judging the level of terrestrial contamination. The near homochirality observed in biological molecules—L-amino acids and D-sugars—is crucial for molecular recognition, enzyme function, information storage, and structure, and is thought to be a property of the origin or early evolution of life.<sup>78</sup> With a few rare exceptions, only L-amino acids are found in biology, while all abiotic syntheses of amino acids result in equal mixtures of L- and D-amino acids unless forces that induce chiral excesses are included. Since there appear to be no biochemical reasons to favor L-amino acids over D-amino acids in enzymes,<sup>79</sup> and early prebiotic chemistry experiments produced only racemic amino acid mixtures, some have argued that the selection of L-amino acid homochirality by life on Earth was random.<sup>80</sup> The origin of homochirality from presumably racemic mixtures in a prebiotic world is a major unsolved question and an area of intense research. The problem contains two parts: (1) establishing an initial imbalance in the two enantiomers; and (2) amplifying that imbalance over time.

An extraterrestrial origin for an initial imbalance between L- and D-amino acids has been proposed based on meteoritic analyses that reveal nonracemic abundances of certain amino acids. In particular, as shown in Figure 7, L-enantiomeric excesses ( $L_{ee}$ ) of up to 21% have been reported for isovaline, a terrestrially rare, nonproteinogenic amino acid, across a wide

range of carbonaceous meteorites.<sup>35,39,41,46,81–84</sup>  $L_{ee}$  of other  $\alpha$ -methyl amino acids have been reported, as have  $L_{ee}$  of isoleucine and  $D_{ee}$  of its diastereomer *allo*-isoleucine.<sup>35,85,86</sup> Analyses of pieces of the Tagish Lake ( $C2_{ungrouped}$ ) meteorite showed large  $L_{ee}$  of  $\sim 99$ , 80, 45, and 55%, respectively, for the protein amino acids threonine, serine, aspartic acid, and glutamic acid,<sup>83</sup> and a racemic composition for the common protein amino acid alanine, suggesting minimal terrestrial biological contamination. Enriched  $^{13}C$  contents of alanine and aspartic acid indicated an abiotic, extraterrestrial origin of these compounds, suggesting that the other amino acids (present at levels below limits of detection for isotopic analysis) may be indigenous to the meteorite as well. These are the largest presumed extraterrestrial enantiomeric excesses for proteinogenic amino acids reported from a meteorite. The racemization half-lives for these amino acids are long compared to the time period of aqueous alteration on the parent body, and it is expected that an L-excess could persist over the 4.5 billion-year lifetime of a meteorite.<sup>87</sup>

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It has been suggested that  $L_{ee}$  measured in meteorites are the result of asymmetric photolytic decomposition of the amino acids or their precursors by polarized radiation in the presolar



**Figure 7.** L-Enantiomeric excesses of the amino acid isovaline of 0 to  $20.5 \pm 7.1\%$  have been measured in carbonaceous chondrites. All data shown here was generated by the authors using the same workup and analysis methods.<sup>39,41,46,47,82,83</sup>

cloud<sup>88</sup> or the effects of spin-polarized secondary electrons.<sup>89</sup> Laboratory experiments have shown that chiral amino acid symmetry breaking and enantiomeric enrichment of up to a few percent can be produced by exposure to ultraviolet circularly polarized light (UV CPL).<sup>90–94</sup> However, polarized light cannot be the sole source of the large enantiomeric enrichments observed, since these enrichments would require photodestruction of  $\gg 99\%$  of the starting materials, requiring impossibly high initial concentrations.<sup>90</sup> Photosynthetic routes by UV CPL<sup>92</sup> minimize the destruction argument, but large  $L_{ee}$  in presolar ices should manifest in  $L_{ee}$  across meteorite classes. The racemic isovaline in CR2 and CR3<sup>39</sup> and large  $L_{ee}$  in CR1<sup>41</sup> meteorites render imbalances induced by UV CPL insufficient to explain the observed enantiomeric excesses. Furthermore, molecular distributions and stable isotope ratios suggest that the  $\alpha$ -amino acids in Murchison and other CM2 meteorites were likely produced during aqueous alteration in their parent body,<sup>16,28</sup> when they would have been shielded from circularly polarized radiation. Therefore, additional amplification mechanisms have been proposed to explain the large  $L$ -isovaline excesses.<sup>95–99</sup>

Probing how amplification of an initial enantiomeric excess in amino acids can occur is a topic of much research in biogenesis.<sup>100</sup> Theoretical work from the mid-20th century proposed the purely chemical mechanism of autocatalytic reactions,<sup>101</sup> but the only experimental corroboration of this concept involves chemistry that has no prebiotic relevance.<sup>96,97</sup> Other proposals involving physical phase behavior or the combination of physical and chemical processes may help to explain the observed extraterrestrial  $L$ -enantiomeric excesses of isovaline and aspartic acid and suspected  $L$ -excesses of glutamic acid and threonine. Unlike alanine, these amino acids can crystallize as enantiopure solids (conglomerates), forming separate crystals containing only  $D$  or  $L$  molecules.<sup>102</sup> A proposed mechanism for the emergence of homochirality from conglomerates supports the idea that amplification of a slight initial  $L$ -excess of these amino acid conglomerate crystals could have occurred during repeated periods of aqueous alteration on the Tagish Lake meteorite parent body.<sup>83,103,104</sup> Observations of larger  $L$ -isovaline excesses in the aqueously altered CI1, CM1, CM2, and CR1 meteorites compared to the less altered CR2 and CR3 meteorites<sup>39</sup> also suggest that aqueous alteration aided the amplification of  $L$ -isovaline excesses on meteorite parent bodies. Large isovaline  $L_{ee}$  ( $\sim 5$  to  $21\%$ ) have also been observed in whole-rock extracts of several metal rich CB and CH3 carbonaceous chondrites.<sup>46</sup> Although it is unclear if high metal content can contribute to the amplification of enantiomeric excesses in these meteorites, the CB and CH chondrites analyzed all contain a mix of both heavily hydrated and anhydrous material, suggesting that an aqueous alteration phase occurred in an asteroidal setting prior to incorporation into the CB and CH parent bodies.<sup>105</sup>

Studies of species related to amino acids may also aid in understanding the origin of enantiomeric excesses, although there are few reported studies of the enantiomeric composition of these meteoritic compounds. Enantiomeric excesses ranging from 3 to 12% for  $L$ -lactic acid have been reported in extracts of Murchison and two CR2 chondrites, with isotopic evidence suggesting that this was not terrestrial contamination.<sup>17</sup> However, these results are complicated by sample losses during workup, which caused measurable isotopic and, potentially, enantiomeric fractionation. Future studies of hydroxy acids in a broader range of meteorites are needed to determine if enantiomeric excesses of hydroxy acids correlate with amino acid excesses.

Some measurements of carboxylic acids and amines have also been reported, with emphasis on structural analogues of isovaline (2-methylbutyric acid and *sec*-butylamine; Figure 6). Isovaline, 2-methylbutyric acid, and *sec*-butylamine contain analogous chiral centers; however, although isovaline has been found to contain an  $L_{ee}$ , only racemic compositions of 2-methylbutyric acid and *sec*-butylamine have been reported in Murchison, Orgueil, and various Antarctic carbonaceous chondrites.<sup>74,75,106,107</sup> Recent anisotropy studies show that UV CPL can induce enantiomeric excesses in amino acids, but not in amines and carboxylic acids,<sup>108,109</sup> perhaps explaining these observations. The contrast between the observed  $L_{ee}$  of isovaline and the racemic nature of its analogous acid and amine suggest that either (1) an initial imbalance was induced in the amino acid enantiomers but not the carboxylic acid or amine; (2) degradation of a chiral amino acid led to loss of stereochemistry at the chiral carbon; (3) racemization occurred in the carboxylic acids and amines at a faster rate than in the amino acids, although the lower acidity of the  $\alpha$ -hydrogen in these compounds argues against this possibility;<sup>110–113</sup> or (4) physical properties of amino acids (e.g., higher polarity) led to the amplification of a small imbalance through aqueous processes inside carbonaceous chondrites.<sup>107</sup> Further studies of these aliphatic compounds from other meteorites may provide additional information on the origins of enantiomeric excesses in amino acids.

The detection of nonracemic amino acids in meteorites suggests that meteoritic delivery to planetary surfaces could have contributed to the origin of homochirality in life on Earth. The observation that only  $L$ -excesses have been found in amino acids containing a single asymmetric carbon in carbonaceous chondrites could indicate that the origin of life on Earth, and possibly elsewhere in our solar system, was biased toward  $L$ -amino acid homochirality prior to the stratification of the solar nebula. Although amino acid homochirality is an important signature of biological processes in the search for evidence of life, the detection of indigenous  $L$ -amino acid excesses in some meteorites indicates that nonbiological processes can lead to significant enantioenrichment for some amino acids, potentially complicating the use of this biosignature for life detection missions and the search for a second genesis.

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## CONCLUSIONS

The study of meteoritic organics has entered a new era with the increased availability of meteorites probing a range of solar system milieus. Highly sensitive and selective laboratory instruments capable of characterizing organics present at low abundances and in small samples maximize the information obtained. Knowledge of the diversity of abundances and structural and enantiomeric distributions in meteorites has expanded as larger data sets have been acquired. Observed heterogeneity in amino acids in meteorites from the same carbonaceous chondrite group, even of the same alteration type, provides evidence that minor changes in reaction conditions can significantly affect the

composition and abundances of the resulting amino acids, a conclusion that surely applies to amino acid synthesis on the early Earth as well. Future work combining meteorite analyses with laboratory experiments, as well as samples returned by missions to solar system bodies, will aid in better understanding the formation and alteration of meteoritic organics and their potential contributions to the origin of life on Earth or elsewhere.

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### Notes

The authors declare no competing financial interest.

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